

BEST AVAILABLE COPY

Remarks

The Applicants have amended Claim 1 by incorporating the subject matter of Claim 2. Claim 2 has accordingly been cancelled. Claim 3 has also been amended to recite that the precipitates of sulfur are formed on the portions of the surfaces of the iron powder by precipitation of sulfur in the iron powder. This is merely a clarifying amendment that naturally follows from the earlier language in that claim regarding precipitates.

Turning now to the merits, the Applicants respectfully submit that the solicited claims are patentable over all of Wolfe '882, JP '401 and Sivavec '927 for the reasons set forth in detail below.

JP '401 is not relevant for several reasons. JP '401 focuses on the removal of P compounds. In that regard, the Applicants agree that JP '401 discloses such removal of P compounds in paragraphs 2, 4 and 8. However, JP '401 in no way concentrates on the removal of halogenated hydrocarbons. Paragraph 4 of JP '401 is a discussion of the prior art, namely JP '288, not a discussion of the capabilities of JP '401. Moreover, that discussion talks about the failure of JP '288 to be able to remove heavy metals and organochlorine compounds. This would lead one of ordinary skill in the art to the belief that JP '288 was incapable of removing organochlorine compounds. However, the remainder of JP '401 focuses on the removal of P compounds, not organochlorine compounds. Accordingly, the Applicants respectfully submit that one of ordinary skill in the art would have no incentive to look to JP '401 for a method of dehalogenating halogenated hydrocarbons when JP '401 teaches those of ordinary skill in the art about removing P compounds.

There is another severe problem with JP '401. This may be found in paragraphs 2, 5 and 24 of JP '401, wherein JP '401 contaminants are reacted with solute iron, derived from iron powder, which forms a sediment and is removed by filtering. Formation of the sediment and removal by filtering can in no way be characterized as dehalogenating the halogenated hydrocarbons as specifically recited in the solicited claims. Removal by filtering and removal by dehalogenation are

utterly different mechanisms and utterly different processes not at all related to one another.

As a consequence, one of ordinary skill in the art would glean from JP '401 that P compounds can be removed by formation of a sediment that is subsequently filtered. This is not what the Applicants claim. The Applicants claim dehalogenation of halogenated hydrocarbons. The Applicants, therefore, respectfully submit that JP '401 is inapplicable under §103 and respectfully request withdrawal of the rejection based on JP '401.

There are still further problems with JP '401. JP '401 fails to teach or suggest the unexpected results achieved by reducing the amount of manganese to about 0.1% or less as claimed herein. There is a general discussion in JP '401 of keeping the manganese content under 2.0 wt% and a limited discussion of keeping the manganese content to less than 0.2 wt%. However, the Applicants note that the voluminous Examples all have an Mn content of 0.20% (excluding the Comparative Examples).

The Applicants respectfully submit that this in no way teaches or suggests a manganese content of about 0.1% or less and, further, in no way teaches or suggests the unexpected results achieved by the Applicants when utilizing such a highly reduced quantity of manganese. To demonstrate this phenomenon, the Applicants enclose an article co-authored by Mr. Nakamaru, an inventor herein, that includes a graph (Fig. 1) showing the effect of sulfur and manganese contents in the iron powder on the dechlorination rate of TCE. Mr. Nakamaru and his colleagues performed several experiments wherein quantities of manganese above 0.1% have degradation times that are drastically higher than the degradation times for iron powders having a manganese content of less than the claimed amount. Specifically, the Applicants invite the Examiner's attention to the graph in the article which shows a degradation time of about 50 hours in the case of the invention and degradation times of about 175 hours up to almost 350 hours when the manganese content is outside of the claimed range. In other words, the degradation time is at least 3½ times higher when

quantities of manganese outside of the claimed range are employed. The Applicants respectfully submit that one of ordinary skill in the art would have no reasonable expectation that reducing the manganese content, based on reading JP '401, would remotely achieve this excellent and unexpected result. The Applicants therefore respectfully submit that JP '401 is inapplicable and further respectfully request withdrawal of the rejection based upon JP '401.

The Applicants respectfully submit that Wolfe is further afield than JP '401 and is inapplicable to the solicited claims. Wolfe fails to disclose, teach or suggest the content of manganese at all, much less the claimed manganese content of about 0.1 wt% or less. The sole reference to manganese appears in Column 6 at line 34, wherein a discussion of commercial iron states that it usually contains carbon, phosphorus, silica, sulfur and manganese. The Applicants agree. What Wolfe fails to disclose, teach or suggest is that 1) manganese is an important element, 2) has a large influence on the process and 3) reducing manganese to about 0.1 wt% or displays unexpected results with respect to the degradation process. As a consequence, the Applicants respectfully submit that one of ordinary skill in the art have no incentive to make modifications to Wolfe that would in any way lead to the invention as recited in the solicited claims.

It must be remembered that, not only must the prior art disclosure contain teachings or suggestions to make modifications, but there must be some reasonable expectation of success that the modifications would cause some benefit. In this case, there are utterly no teachings in that regard. Manganese is mentioned in one location as a mere afterthought and there is utterly no consideration given to it as an important constituent, that its content should or could be controlled and that the unexpected benefits discovered the Applicants would occur. The Applicants accordingly respectfully request withdrawal of Wolfe.

The Applicants respectfully submit that Sivavec is even further afield than Wolfe. Careful scrutiny of the entire Sivavec disclosure reveals that not one word about manganese is presented.

It is therefore non-enabling as prior art. Careful scrutiny of the entire Sivavec document reveals that there are no teaching or suggestions to those of ordinary skill in the art concerning the importance of manganese, that its contents should be controlled and that having about 0.1 wt% or less of manganese would produce the unexpected results discovered by the Applicants. Withdrawal of Sivavec is respectfully requested.

The Applicants also note that Sivavec fails to disclose, teach or suggest the amount of sulfur in the iron powder. While it is true that Sivavec teaches the amount of FeS_2 in an amount of 1 – 30% at Column 3, line 47, for example, this does not disclose the sulfur content in the iron powder to those of ordinary skill in the art. FeS_2 is not iron powder, either literally or in the context of Sivavec. Sivavec specifically refers to iron powder separately from FeS_2 . Thus, Sivavec also fails to disclose, teach or suggest the amount of sulfur actually contained within the iron powder. For this reason as well, Sivavec is also inapplicable to the solicited claims. Withdrawal of Sivavec is respectfully requested.

The Applicants also submit three publications mentioned in a European Search Report and submit those publications in an IDS. Partial translations are also enclosed.

Finally, the Applicants submit this Amendment together with a Request for Continued Examination. Entry into the Official File of the above amendments, consideration of the above statements in favor of patentability and early allowance of the claims is respectfully requested.

Respectfully submitted,



T. Daniel Christenbury
Reg. No. 31,750

TDC:lh
(215) 656-3381



Effect OF THE MICROSTRUCTURE OF AN IRON POWDER ON THE REACTIVITY WITH TRICHLOROETHYLENE

Hiroki Nakamaru, Tomoshige Ono, Yoshiei Kato, and Kuniaki Ogura

Technical Research Laboratories, Kawasaki Steel Corporation, 1, Kawasaki-cho, Chuo-ku,
Chiba 260-0835, Japan

Introduction

Reductive degradation of chlorinated hydrocarbons in aqueous solutions by zero-valent iron is affected by many factors. Surface condition of the iron may affect on the process as well as solution condition such as pH, dissolved oxygen, anion species, and conductivity (Senzaki and Kumagai, 1988) and the kind of chlorinated hydrocarbons (Gillham and O'Hannesin, 1994).

Importance of the surface area has repeatedly emphasized (e.g., Matheson and Tratnyek, 1994; Sivavec and Horney, 1995). However since only a limited part of the iron surface works as reactive sites (Concept of Fractional Active Site Concentration: Gotpagar, Grulke, and Bhattacharyya, 1998), and the fraction of reactive sites may be specific character in each iron from different sources, it might not accurate to predict a difference in reactivity of some irons by comparison of surface area. What is important is not how huge the surface area measured by BET analysis on which the nitrogen gas physically adsorbed, but how many active sites for the chemical reactions exist on the surface of the iron.

It is well known that by coupling with more noble metallic elements than iron, e.g., Pd (Muftikian, Fernando and Korte, 1995), Ni (e.g., Sweeney, 1983; Senzaki, 1991; Sivavec, Mackenzie and Horney, 1997; Fennelly and Roberts, 1998), Cu (e.g., Sweeney, 1983; Senzaki, 1991; Fennelly and Roberts, 1998), etc. (e.g., Odziemkowski, Gillham, and Focht, 1998; Ho, Orth, and Mackenzie, 1997), reactivity of the iron powder for reductive dechlorination of chlorinated hydrocarbons is improved. The role of these noble metallic elements may be a hydrogen generator or a direct electron translator from a metallic phase to chlorinated hydrocarbons adsorbed on the surface. Either as a hydrogen generator or as a direct electron translator, these elements contacting on the iron must work as a local cathode while the iron works as local anode.

By pretreatment with NaCl solution, reactivity of iron was improved (Gotpagar, Lyuksyutov, Cohn, Grulke and Bhattacharyya, 1999) and the defects/abnormalities present on the surface of the iron were hypothesized to contribute to the reactive sites. In this case, defects/abnormalities may also works as local cathode.

All these things mentioned above indicate that another phase contacted with iron could potentially be a local cathode and promote the reductive dechlorination reactions. The second phase material would preferably be conductive unless it does not work as an electrode. In this work, we tried to observe the effect of the microstructure of an iron powder prepared by water spray atomize process, that is common in producing a commercial base iron powder for the powder metallurgy.

Material and Method

Iron powders:

The reagent grade iron powder was purchased from Wako Jyunyaku Corporation as a reference specimen. Another reference specimen was the KIP301A water atomized iron powder produced by Kawasaki Steel Corporation. Some kind of iron powders were prepared by laboratory water atomized

4

process, and then heated in the dry hydrogen gas stream for one hour at 1073K. Sulfur and manganese composition of the laboratory atomized iron powders were changed.

Batch dechlorination test

An electrolyte solution containing 40mg/L of CaCO_3 and 80mg/L of Na_2SO_3 was prepared using MilliQ de-ionized water. 5g of each iron powder was added to each 100mL volume glass vial bottle, that was then filled with 50mL of the electrolyte solution, then TCE was spiked to ensure the initial concentration in the solution was 5mg/L. The bottles were sealed immediately with aluminum crimp caps with Teflon-lined butyl rubber septa. The bottles were then shake to the longitude direction by 3 Hz under the constant temperature of 296K. By certain intervals, aliquot of the solution was sampled and the concentration of TCE in the solution was determined by the headspace GC/MS analysis method.

Results and Discussion

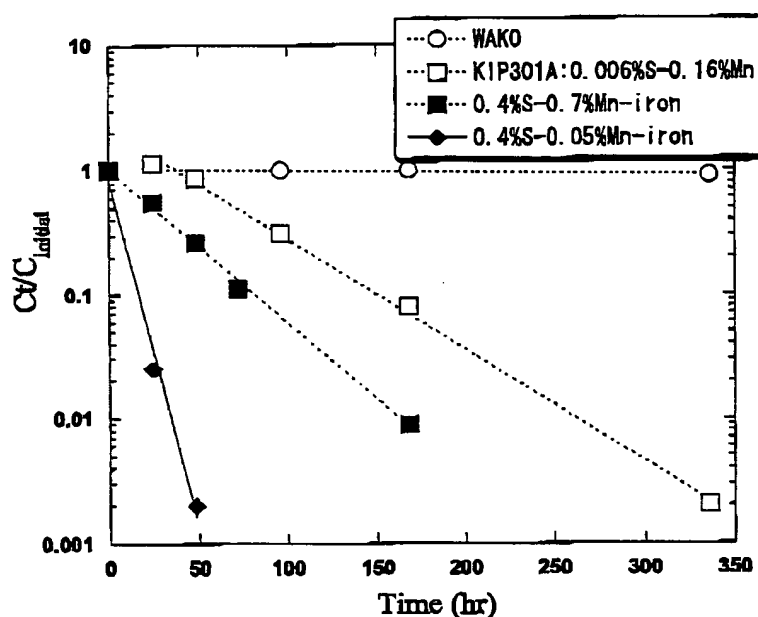


Fig. 1 Effect of the sulfur and manganese contents in the iron powder on the dechlorination rate of the TCE.

Increasing the sulfur contents in the atomized iron powder resulted in improving the TCE degradation rate. However, with higher manganese contents, effect of sulfur content was not so drastic. In case of the iron powder with manganese contents 0.7%, sulfur and manganese were detected at the same area (Fig. 2). Conductivity of MnS is by two orders lower than the conductivity of the FeS , thus in case of MnS , the second phase deposited on the surface of the base iron hardly works as local cathode.

In the experiment, the result of which is shown in Fig. 3, two kinds of laboratory atomized iron powders were sieved. The different surface area of each iron powder was obtained by sieving. The relationship between the degradation rate constant of the TCE and the surface area was linear in each iron powder. However, higher surface area doesn't mean higher rate constant if the different type of iron powder was compared each other. The result shows the simple compare of BET surface areas between different kinds of iron powder means nothing.

5

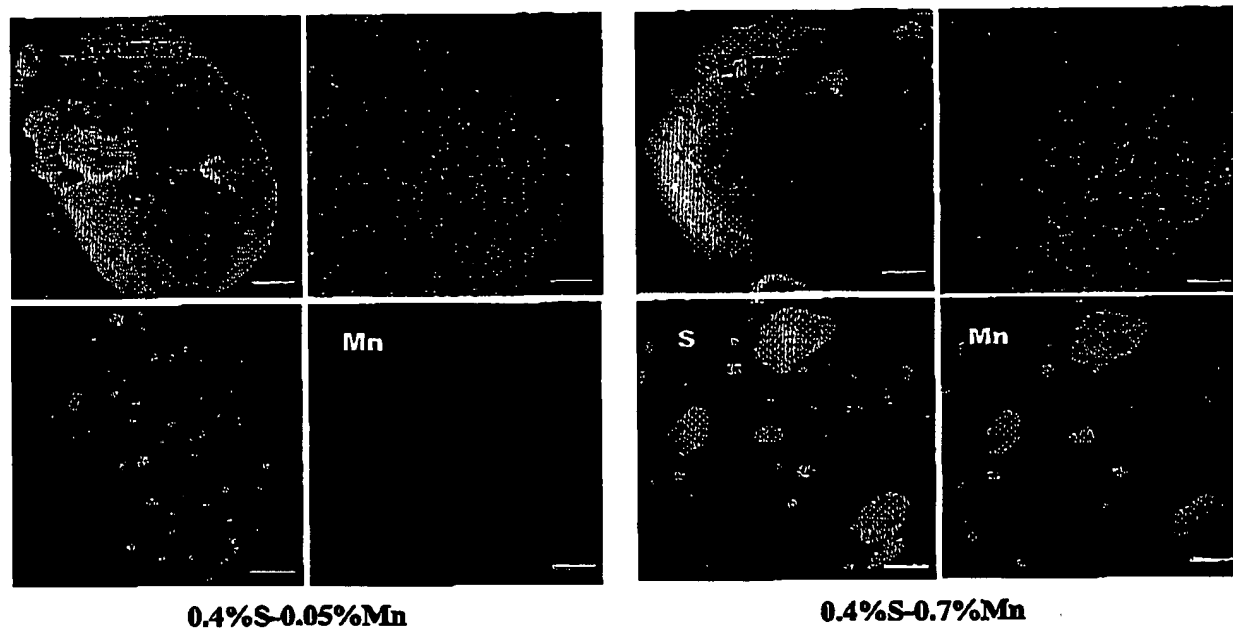


Fig. 2 EPMA analysis of the surface for the laboratory atomized iron powders

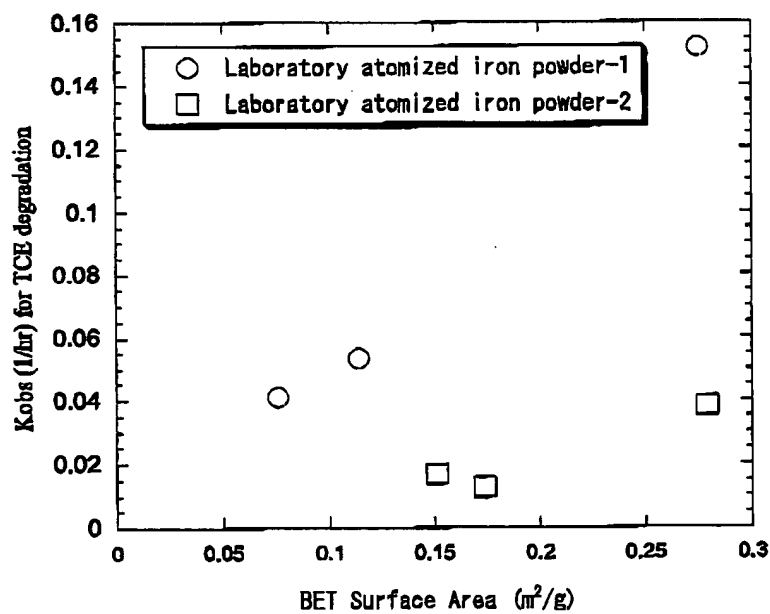


Fig. 3 Effect of the surface area of the iron powder on the TCE degradation rate.

References Cited

- Fennelly, J.P., and Roberts, A.L. 1998. "Reaction of 1,1,1-Trichloroethane with Zero-Valent Metals and Bimetallic Reductants" *Environ. Sci. Technol.*, 32 (13), 1980-1988.
- Gillham, R. and O'Hannesin, S. 1994. "Enhanced Degradation of Halogenated Aliphatics by Zero-Valent Iron" *Ground Water*, 32 (6), 958-967.
- Gotpagar, J., Grulke, E., and Bhattacharyya, D. 1998. "Reductive Dehalogenation of Trichloroethylene: Kinetic Models and Experimental Verification" *J. Haz. Mater.*, 62, 243-264.
- Gotpagar, J., Lyuksyutov, S., Cohn, R., Grulke, E., and Bhattacharyya, D. 1999. "Reductive Dehalogenation of Trichloroethylene with Zero-Valent Iron: Surface Profiling Microscopy and Rate Enhancement Studies" *Langmuir*, 15 (24), 8412-8420.
- Ho, S.V., Orth, R.G. and Mackenzie, D.E. 1997. "Dehalogenation of Halogenated Hydrocarbons in Aqueous Compositions" International Patent Application No. WO97/04868.
- Matheson, L.J. and Tratnyek, P.G. 1994. "Reductive Dehalogenation of Chlorinated Methanes by Iron Metal" *Environ. Sci. Technol.*, 28 (12), 2045-2053.
- Muftikian, R., Fernando, Q., and Korte, N. 1995. "A Method for the Rapid Dechlorination of Low Molecular Weight Chlorinated Hydrocarbons in Water" *Water Res.*, 29 (10), 2434-2439.
- Odziemkowski, M.S., Gillham, R.W., and Focht, R. 1998. "Electroless Hydrogenation of Trichloroethylene by Fe-Ni(P) Galvanic Couples" *Electrochem. Soc. Proceedings*, 98 (5), 91-102.
- Senzaki, T., and Kumagai, Y. 1988. "Reductive Degradation of Chlorinated Organic Hydrocarbons by Iron Powder" *Kogyosui*, 357, 2-7.
- Senzaki, T. 1991. "Reductive Degradation of Trichloroethylene by Iron Powder II" *Kogyosui*, 391, 29-35.
- Sivavec, T. and Horney, D.P. 1995. "Reductive Dechlorination of Chlorinated Ethenes by Iron Metal" *Prepr. Pap. ACS Natl. Meet., Am. Chem. Soc., Div. Environ. Chem.*, 35(1), 695-698.
- Sivavec, T. and Horney, D.P. 1996. "Method for Destruction of Halogenated Hydrocarbons" US Patent No. 5,575,927.
- Sivavec, T.M., Mackenzie, P.D., and Horney, D.P. 1997. "Effect of Site Ground Water on Reactivity of Bimetallic Media: Deactivation of Nickel-Plated Granular Iron" *Prepr. Pap. ACS Natl. Meet., Am. Chem. Soc., Div. Environ. Chem.*, 37 (1), 83-84.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.